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Calibration of elemental and isotope proxies by inorganic precipitation experiments

Abstract

The main focus of my PhD study is to constraint laboratory experiments in order to refine established elemental and isotopic proxies in carbonate minerals, which are used to reconstruct environmental conditions at the time of formation. Therefore, the present literature study refers to carbonate precipitation experiments with special regard to the incorporation behavior of distinct cations. Rapid precipitation rates can also promote the incorporation of foreign ions into the solid phase [1]. Prominent examples of these paleo-environmental proxies are for instance, the incorporation of magnesium in calcium carbonates to identify continental weathering, dolomitization and hydrothermal activity [2; 3; 4] or the strontium content as indicator of the sea surface temperature at time of formation [5; 6; 7; 8]. In turn, isotopic proxies like the isotopes of lithium provide information about past weathering and past temperature changes of the deep-ocean [9; 10; 11], whereas boron isotopes are used to determine seawater paleo-pH [12; 13; 14]. As most of these proxies were determined from natural samples, where a detailed knowledge about the physicochemical parameters is scarce, e.g., the influence of organics on the incorporation of cations, constraint laboratory experiments are in need for evaluation and most importantly calibration of such proxies. Accordingly, experiments like co-precipitation of elements with carbonate minerals, such as calcite and aragonite, are conducted in controlled environments by using diffusion and mixing techniques as well as flow-through systems mimicking natural systems [4; 5; 14; 15; 16; 17; 18; 19; 20; 21; 22].

Introduction

Past environmental conditions can be reconstructed using the trace elemental and isotopic ratio of carbonate minerals as environmental proxies [9]. The exchange behavior of elements and stable isotopes in the crystal lattice of carbonate minerals are particularly sensitive to environmental settings. The most readily replacing cations for Ca^{2+} in calcite and/or aragonite are Mg^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+} and Ba^{2+} [5; 16; 22; 23; 24; 25]. Magnesium is the most abundant divalent cation in the ocean, which is used to characterize the effect of different physical and chemical parameters such as temperature, pressure and pH [16; 18; 26; 27]. Mg isotopes are a tracer of continental weathering, dolomitization and hydrothermal activity [2; 3]. Sr incorporation into calcium carbonates reflects the environmental conditions during mineral growth and can thereby be used as proxy to reconstruct the prevailing paleo conditions. Additional to divalent cations as replacement for Ca^{2+}, monovalent ions are getting incorporated into carbonates as well [5; 6; 7; 8]. For instance, lithium originating from rivers and from high-temperature hydrothermal circulation systems ends up in the ocean and consequently gets incorporated in marine sediments. These sediments are enriched in Li even relative to their continental precursors or relative to sediments originating from low-temperature basalt alteration [28]. Lithium in carbonates provides an archive for past environmental conditions in two aspects: First, the inverse temperature dependence of the Li/Ca ratio in calcite, especially at low temperatures, can be used as a tool to investigate past temperature changes in the deep-ocean. Second, the suggested lack of temperature dependence of Li-isotope fractionation during its incorporation into calcite shows that carbonate minerals could be used as signal of δ^7Li of natural waters to provide information about the intensity of global hydrothermal circulation or past weathering of continents [9; 10]. Boron isotopes as another example for incorporation into calcium carbonates show a correlation to seawater paleo-pH as

isotope fractionation between the boron-bearing species in seawater, boric acid $B(OH)_3$ and borate ion $B(OH)_4^-$, exists and their specific concentrations change as a function of pH [12; 13].

Experimental approaches

I.   CO$_2$ diffusion method - Incorporation of Sr^{2+} and Ba^{2+} into calcite and aragonite

This experimental setup of the CO_2-diffusion technique is used to precipitate e.g. calcite. A polyethylene (PE) bottle with a membrane is placed into a vessel of an outer solution (Fig. 1). The inner solution consists of a $NaHCO_3$ solution and is saturated with CO_2 gas. The outer solution exhibits significantly lower pCO_2 values and contains $CaCl_2$ and NH_4Cl. As the experiment proceeds, CO_2 diffuses through the membrane from the inner to the outer solution due to the CO_2 gradient between both solutions and reacts with Ca^{2+} to precipitate calcite. In the outer solution a constant pH is kept by pH-stat titration using a NaOH solution. The concentration of dissolved inorganic carbon (DIC) in the outer solution increases until a critical saturation for spontaneous calcite precipitation is reached. The precipitation rate of calcite thereby is controlled by the flux of CO_2 through the membrane. The CO_2 flux is adjusted by the thickness of the membrane and the pH of the inner and outer solution. During the whole run of the experiment the outer solution is stirred to assure that calcite is growing from a homogeneous solution [5; 15; 16; 17]. The precipitation of calcite induced by diffusion of CO_2 can be described by the following reaction: $Ca^{2+} + CO_2 + OH^- \leftrightarrow CaCO_3 + H^+$ [16]. In other experiments, the outer solution is dopped with Sr^{2+} traces, in the form of $SrCl_2$, to investigate the incorporation of Sr^{2+} into calcite during its precipitation [5; 15]. The above described experimental approach is also used to investigate the co-precipitation of Sr^{2+} and Ba^{2+} with aragonite. The inner solution consists of the same components than in the calcite precipitation experiment. But the outer solution involves $CaCl_2$ and MgCl with Sr^{2+} and Ba^{2+} traces. Strontium (Me^{2+} $= Sr^{2+}$) and barium ($Me^{2+} = Ba^{2+}$) are incorporated into aragonite according to the reaction: $xCa^{2+} + (1 - x)Me^{2+} + CO_3^{2-} = Ca_xMe_{(1-x)}CO_3$ [16].
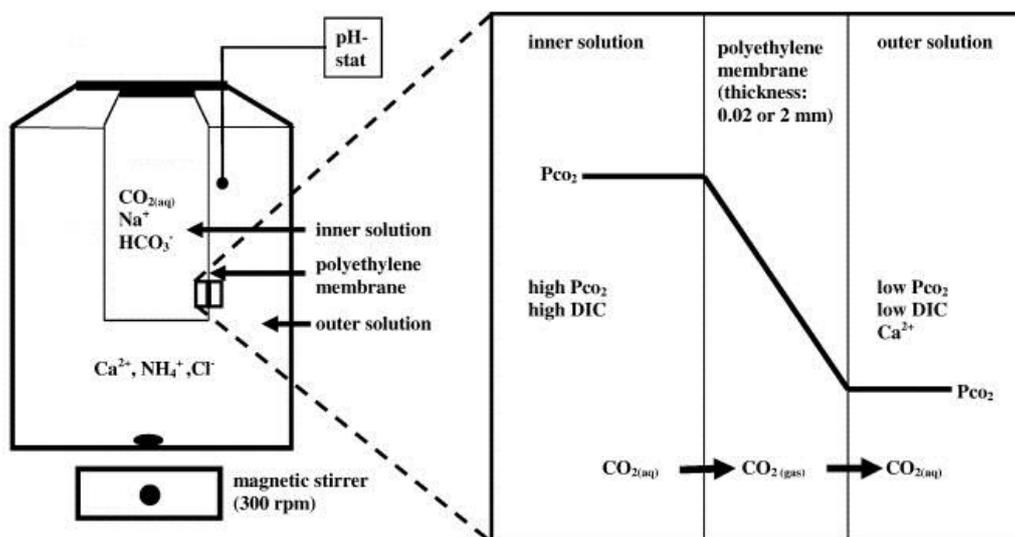

Figure 1: Experimental setup for the crystallization of calcite using CO_2 diffusion technique [16]

II.   Mixing approach at chemical-state conditions - Incorporation of Ba^{2+}, Mg^{2+}, lithium and boron into calcite and aragonite

The reactor solution in this experiment (Fig. 2) contains a $MgCl_2$ solution and calcite seeds. The pCO_2 and the pH are maintained constant by bubbling CO_2 gas into the reactor. A thermostatic bath is holding the temperature constant in the reactor. Two separate solutions of $(Ca,Mg)Cl_2$ and Na_2CO_3 are pumped into the reaction vessel by using a peristaltic pump. The precipitation rate can be modified by changing the flow rate or changing the molalities of the inlet solutions. Every 24 h, a

volume of the reactive solution equal to the volume of the inlet solutions added in 24 h by the peristaltic pump, is sampled with a syringe [4]. For the co-precipitation of boron, a reactor solution of H_3BO_3 with calcite or aragonite seeds is used. The two inlet solutions involve $CaCl_2$ and $Na_2CO_3 - H_3BO_3$, which are pumped into the reaction vessel [14].
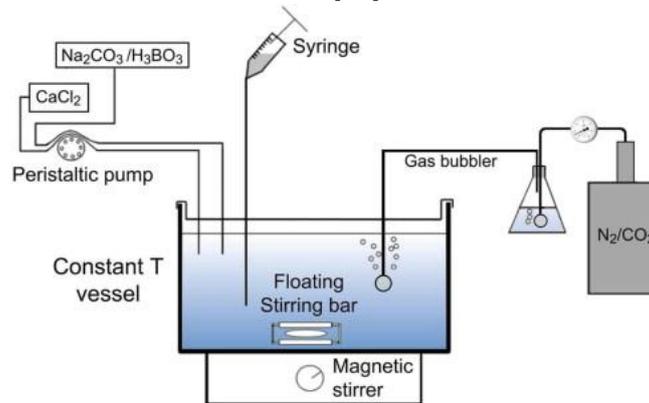

Figure 2: Experimental setup for the incorporation of boron in calcite and aragonite [14]

III.   Cr(VI)-calcite co-precipitation in double diffusion silica hydrogel

To co-precipitate Cr(VI)-calcite the calcium carbonate is synthesized using a double diffusion system (Fig. 3). This design consists two vertical branches filled with solutions of $CaCl_2$ and Na_2CO_3 separated by a column of silica hydrogel, which is spiked with different amounts of Cr(VI) solution. The gelation process takes 1 to 2 h by adding HCl to a sodium silicate solution until a pH of 5.5 is reached. After the gelation process, the reactants are brought together by diffusing through the silica hydrogel, subsequently followed by crystal growth within the gel column. The crystals are extracted by dissolving the gel in a NaOH solution and rinsing with ultrapure water [29; 30]. The advantage of this technique is to form large crystals and to precipitate a wide range of solid solution composition. The disadvantage is that results cannot be directly correlated to e.g. incorporation data using aqueous solutions as significant concentrations gradient in respect to dissolved components have to be considered in the gel pore solution and in the case of isotopes, complex isotope fractionation processes caused by sorption processes and aqueous diffusion occur [31].
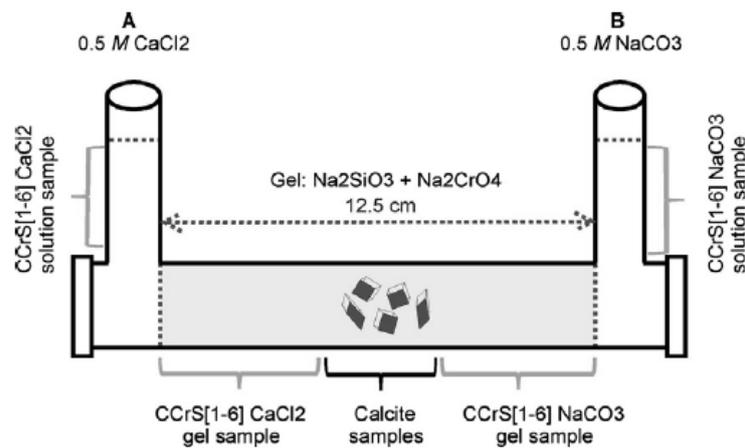

Figure 3: Schema of calcite crystal precipitation in double diffusion silica hydrogel [29]

Outlook

Although, a lot of different studies about the incorporation and co-precipitation of elements and their isotope systems exist, there are still open questions:

- Which element and isotopic system are useful as a proxy to reconstruct the seawater composition?
- Under which condition occurs incorporation and co-precipitation of these elements (e.g. precipitation rate, pH, temperature)?
- How are these elements incorporated into the respected structure?
- Under which condition isotope fractionation of these elements occurs?
- Which kinetic effects produce incorporation of lighter or heavier isotopes?

Therefore, we want to go beyond existing methods, developing new experimental approaches and using new proxies like clumped, lithium or chromium isotopes.

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